Transmission secondary ion mass spectrometry using 5MeV C60[+] ions

AUTHOR(S):

Nakajima, K.; Nagano, K.; Suzuki, M.; Narumi, K.; Saitoh, Y.; Hirata, K.; Kimura, K.

CITATION:

Nakajima, K. ...[et al]. Transmission secondary ion mass spectrometry using 5MeV C60[+] ions. Applied Physics Letters 2014, 104(11): 114103.

ISSUE DATE:

2014-03-17

URL:

http://hdl.handle.net/2433/187036

Transmission secondary ion mass spectrometry using 5MeV C60 + ions

K. Nakajima, K. Nagano, M. Suzuki, K. Narumi, Y. Saitoh, K. Hirata, and K. Kimura

Citation: Applied Physics Letters **104**, 114103 (2014); doi: 10.1063/1.4868655
View online: http://dx.doi.org/10.1063/1.4868655
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/11?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **104**, 114103 (2014)

Transmission secondary ion mass spectrometry using 5 MeV C_{60}^+ ions

K. Nakajima,[1] K. Nagano,[1] M. Suzuki,[1] K. Narumi,[2] Y. Saitoh,[2] K. Hirata,[3] and K. Kimura[1,a)]
[1]*Department of Micro Engineering, Kyoto University, Kyoto 615-8540, Japan*
[2]*Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency, 1233 Watanuki-machi, Takasaki, Gumma 370-1292, Japan*
[3]*National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

(Received 8 February 2014; accepted 5 March 2014; published online 17 March 2014)

In the secondary ion mass spectrometry (SIMS), use of cluster ions has an advantage of producing a high sensitivity of intact large molecular ions over monatomic ions. This paper presents further yield enhancement of the intact biomolecular ions by measuring the secondary ions emitted in the forward direction. Phenylalanine amino acid films deposited on self-supporting thin Si_3N_4 films were bombarded with 5 MeV C_{60} ions. Secondary ions emitted in the forward and backward directions were measured. The yield of intact phenylalanine molecular ions emitted in the forward direction is significantly enhanced compared to the backward direction while fragment ions are suppressed. This suggests a large potential of using transmission cluster ion SIMS for the analysis of biological materials. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868655]

There has been an increasing demand to extend accessible mass range in secondary ion mass spectrometry (SIMS) particularly for biological and biomedical molecular imaging.[1,2] During the past two decades, various kinds of large clusters, such as C_{60} ions,[3] argon gas cluster ions,[4] water cluster ions,[5] and metal cluster ions,[6] have been used as primary ions. It was shown that these cluster ions enhance emission of intact large molecular ions compared to monatomic ion bombardment.

In SIMS, secondary ions emitted from a sample in the backward direction with respect to the direction of a primary ion are generally measured. If a specimen of a self-supporting thin film is used, the secondary ions emitted in the forward direction upon transmission of the primary ions can also be measured. So far, there have been only few studies about the transmission SIMS.[7,8] Boussofiane-Baudin *et al*. found enhancement of secondary ion yield in the forward direction compared to the backward direction.[7] The origin of the enhancement was suggested to be the larger stopping power at the exit surface due to higher charge states achieved during the passage. Because the projectiles can directly transfer their momentum to the target atoms in the forward direction there might be further enhancement in the forward direction in addition to their proposed mechanism. Thus, cluster ion SIMS in combination with the geometry of forward emission may be a promising technique to enhance the yield of intact large molecular ions. However, there has been almost no attempt to measure secondary ions emitted by large cluster ions in the forward direction. This is because the energy of the primary cluster ions used in SIMS is typically several tens of keV. These ions cannot penetrate through a specimen, unless the specimen is extremely thin. For example, the projected range of 30 keV C_{60} ions in silicon is only 6.7 nm.[9] In the transmission geometry, cluster ions of much higher energies are required.

In the present paper, we employ 5 MeV C_{60}^+ ions to measure secondary ions emitted in the forward direction from phenylalanine amino acid films deposited on self-supporting amorphous Si_3N_4 (a-Si_3N_4) films. We found significant enhancement of the intact phenylalanine ion yield and suppression of fragment ions in the forward direction compared to the backward direction. The origin of the observed enhancement and suppression is discussed in terms of the density distribution of the deposited energy.

Phenylalanine amino acid was purchased from Nakalai Tesque (Japan) and used without further purification. Self-supporting a-Si_3N_4 films (1.5×1.5 mm^2) of thickness 20–50 nm made by low pressure chemical vapor deposition were purchased from Silson Ltd (Northampton, UK). Thin films of phenylalanine (20–100 nm) were prepared on the a-Si_3N_4 films using vacuum evaporation. The thickness and uniformity of the deposited phenylalanine films were estimated by measuring energy loss spectra of 6 MeV Cu^{4+} ions passing through the phenylalanine/a-Si_3N_4 films.

A beam of 5 MeV C_{60}^+ ions was produced by a 3 MV tandem accelerator at JAEA/Takasaki. The beam was collimated by an aperture (diameter 1 mm) and sent to a scattering chamber (base pressure 1×10^{-6} Pa). For the SIMS measurements, the beam current was reduced to less than 0.1 fA. The collimated beam was incident on the phenylalanine/a-Si_3N_4 film from the a-Si_3N_4 side at 45° with respect to the surface normal. The ions passing through the film were detected by a silicon surface barrier detector of 20 mm diameter which was placed about 110 mm downstream from the specimen. Positive secondary ions emitted in the forward direction from the phenylalanine films were accelerated by a mesh electrode biased at −0.7 kV and detected by a micro-channel plate (MCP) after traveling through a drift tube of 930 mm length. The timing of the projectile and secondary ion signals were measured by a 4ch time-to-digital converter (WE7521: Yokogawa Electric Corp., time resolution 5 ns) and the data was stored in a list mode. About 5×10^5 events were acquired for each measurement. We also measured the secondary ions

a)E-mail: kimura@kues.kyoto-u.ac.jp

emitted in the backward direction from the phenylalanine film. In this backward measurement, the drift tube and MCP were moved behind the sample (135° with respect to the beam direction) and the phenylalanine/a-Si_3N_4 film was rotated by 180° so that the secondary ions emitted from the entrance surface of the phenylalanine film can be measured. For comparison, similar measurements were performed with 6 MeV monatomic Cu^{4+} ions produced by a 1.7 MV tandetron accelerator at Kyoto University. In the following, we will first present and discuss the results of 6 MeV Cu^{4+}.

Figure 1 shows the observed mass spectra of positive secondary ions emitted in the forward (solid line) and backward (dashed line) directions when 6 MeV Cu^{4+} ions are incident on the phenylalanine(90 nm)/a-Si_3N_4(50 nm) film. A peak of protonated intact phenylalanine ions $[M+H]^+$ is seen at m/z = 166. There are also many peaks corresponding to fragment ions, for example, $[M\text{-}COOH]^+$ ions at m/z = 120, $C_8H_8^+$ ions at m/z = 104, $C_7H_7^+$ ions at m/z = 91, $C_6H_5^+$ ions at m/z = 77, and so on. Both spectra are similar but the secondary ion yields are slightly enhanced in the forward direction. For example, the ratio of the forward to backward yield is ~1.2 for $[M+H]^+$.

Similar enhancement of the secondary ion yield in the forward direction was observed by Boussofiane-Baudin *et al.*[7] They observed protonated phenylalanine ions emitted in the forward and backward directions from a phenylalanine film deposited on a self-supporting carbon foil irradiated with 4–14 MeV Au^+ ions. The ratio of the forward to backward yield observed by them was ~1.6. The origin of the observed enhancement was suggested to be the difference in the stopping power between the entrance and exit surfaces. During the passage through the film, the charge state of the Au ions increases from 1+ to the equilibrium charge state, which is about 9+ for 7 MeV Au ions. Thus, the stopping power at the exit surface is larger than the entrance surface. Consequently, the secondary ion yield becomes larger in the forward direction. The present enhancement of the forward yield may be explained by this scenario. In order to confirm this, the transmitted Cu ions were resolved into their charge states using a dipole magnet and TOF spectra were measured for each charge state. The mean charge state of the transmitted Cu ions was measured to be 8.5+, which is about twice larger than the incident charge state (4+). Figure 2 shows the dependence of the $[M+H]^+$ yield on the exit charge state. As is expected, the observed yield increases with charge state, confirming that the enhancement of secondary ion yield in the forward direction is ascribed to the charge state difference between the entrance and exit surfaces.

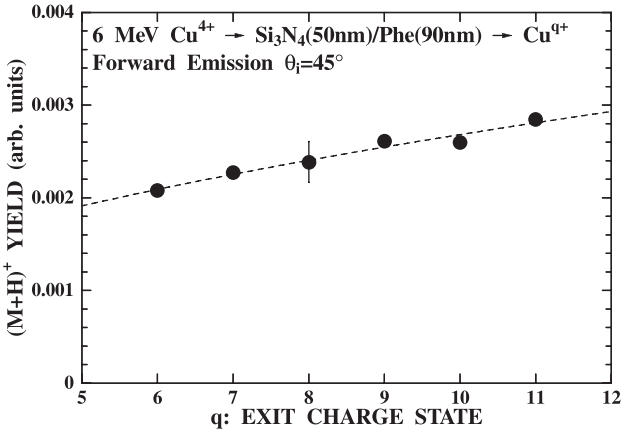

FIG. 2. The yield of the protonated intact phenylalanine ion emitted in the forward direction under 6 MeV Cu^{4+} ion bombardment as a function of exit charge state. A typical error bar is also shown.

The ratios of the forward to backward yield for various fragment ions together with the intact molecular ion are plotted as a function of mass number in Fig. 3 (triangles). The ratio increases with decreasing mass number, indicating that yield enhancement in the forward direction is more pronounced for fragment ions. This behavior may also originate from the difference in the stopping power between the entrance and exit surfaces. There is a general consensus that the fragment ions are emitted mainly from the central region (infratrack), where the density of the deposited energy is high, while intact molecules are emitted mainly from the outer region (ultratrack) as is schematically shown in Fig. 4(a).[10,11] In the case of larger stopping powers (higher charge states), the density distribution of deposited energy is higher and broader than the case of smaller stopping powers (see Fig. 4(b)). As a result, both the central and outer regions

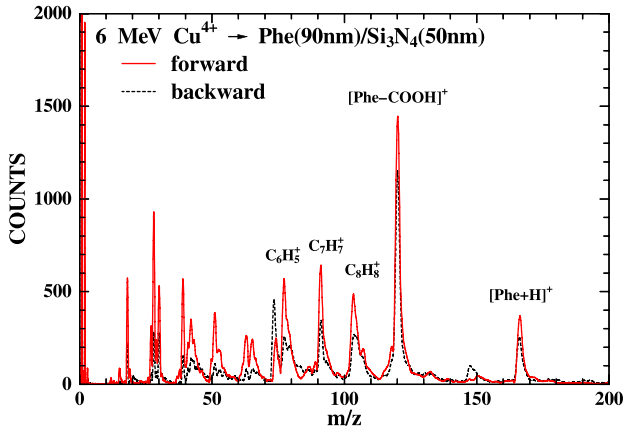

FIG. 1. Mass spectra for positive ions from phenylalanine films on a-Si_3N_4 films under 6 MeV Cu^{4+} ion bombardment. The spectra observed in the forward direction (solid line) and in the backward direction (dashed line) are shown.

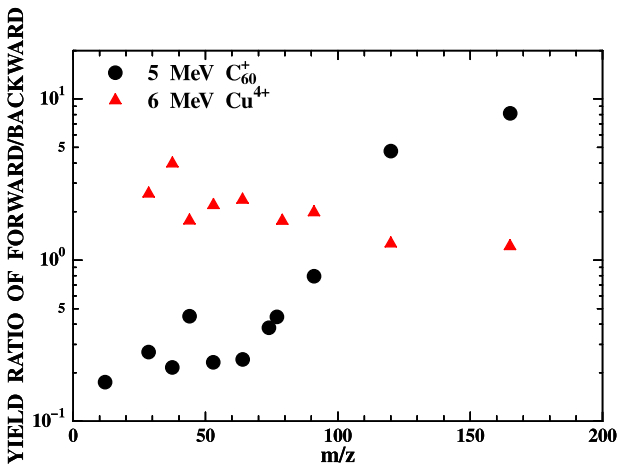

FIG. 3. The ratio of the forward to backward yield as a function of mass number. The results for 5 MeV C_{60}^+ (●) and 6 MeV Cu^{4+} bombardment (▲) are shown.

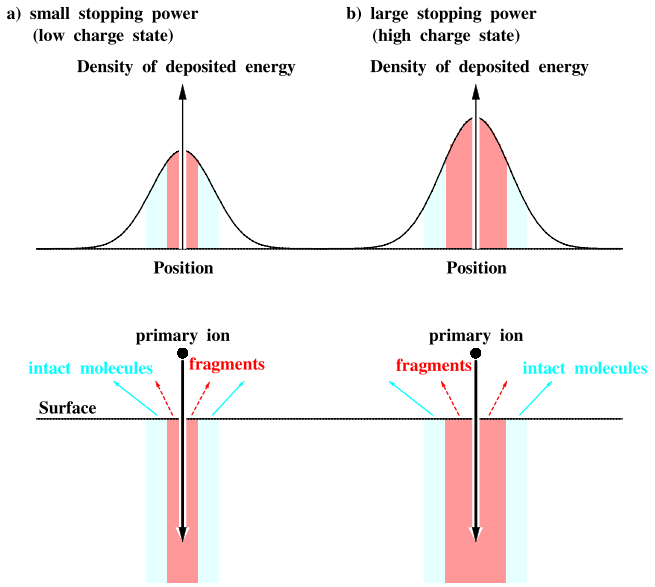

FIG. 4. Spatial distributions of the deposited energy at the target surface for the cases of (a) large stopping power and (b) small stopping power are schematically shown. In the central region (heavily hatched area) fragmentation is dominant, while intact molecular ions are preferentially emitted from the outer region (lightly hatched area).

are wider but the increase of the central region is more pronounced as is schematically shown in Fig. 4(b). Consequently, the yield of the fragment ion increases more rapidly with increasing stopping power (charge state) than the intact molecular ion.

Figure 5 shows the mass spectra of positive secondary ions emitted in the forward (solid line) and backward (dashed line) directions observed using 5 MeV C_{60}^{+} ions. Although the projectile energy is comparable to 6 MeV Cu^{4+} ions the observed secondary ion yield is much larger. The $[M+H]^{+}$ yield is 4.7×10^{-3} ions/incident ion in the backward direction, which is about 4 times larger than that for 6 MeV Cu^{4+} ions. The enhancement is more pronounced in the forward direction. The $[M+H]^{+}$ yield is 3.9×10^{-2} ions/incident ion which is 8 times larger than the backward direction. It is also noteworthy that the yield of the fragment ions are suppressed in the forward direction compared to the backward direction. Figure 3 shows the forward to backward yield ratio as a function of the mass number of the secondary ion (circles). The ratio is about 0.2 for smaller fragment ions and increases very rapidly with mass number. Interestingly, this behavior is opposite to the case of 6 MeV Cu^{+} ions.

During the passage of C_{60}^{+} through the target foil, the constituent carbon atoms are subject to scattering. As a result, they separate from each other and distribute in a wider region. The broadening of the spatial distribution due to the multiple scattering was estimated using the SRIM code.[12] Figure 6 shows the obtained spatial distribution of constituent carbon ions at the exit surface of the sample (a-Si_3N_4(20 nm)/phenylalanine(99 nm)). The FWHM of the distribution is about 47 nm, which is about 70 times larger than the diameter of C_{60}^{+}. Note that the carbon ions are also subject to the Coulomb explosion, but the expected broadening due to the Coulomb explosion is only 6 nm, indicating that the distribution is mainly determined by the multiple scattering. Thus, at the exit surface, the deposited energy distributes in a large area with a relatively low peak density. This is a preferable situation for the emission of intact molecular ions. On the contrary, at the entrance surface, the deposited energy concentrates in a narrow area, which results in intense fragmentation of target molecules. Thus, the intact molecular ion is pronounced in the forward direction and the fragment ions are pronounced in the backward direction as was observed. In passing, the bias voltage of the MCP entrance was as low as −1 kV with respect to the target (i.e., the energy of secondary ion was 1 keV) in the present measurement due to the instrumental limitation. Thus, the efficiency of MCP might be low especially for heavy ions. This means the absolute secondary ion yields measured in the present paper are slightly meaningless (real yields might be larger). The forward to backward ratio, however, is not affected by the possible low efficiency. The measurement of the absolute yield is now in progress.

Finally, we mention that a small peak seen at m/z ∼ 149 shows a slightly strange behavior. The yield is much stronger in the backward direction compared to the forward direction for 6 MeV Cu^{4+} (see Fig. 1), while it is opposite for 5 MeV C_{60}^{+} (see Fig. 4). The origin of this strange behavior is not clarified yet.

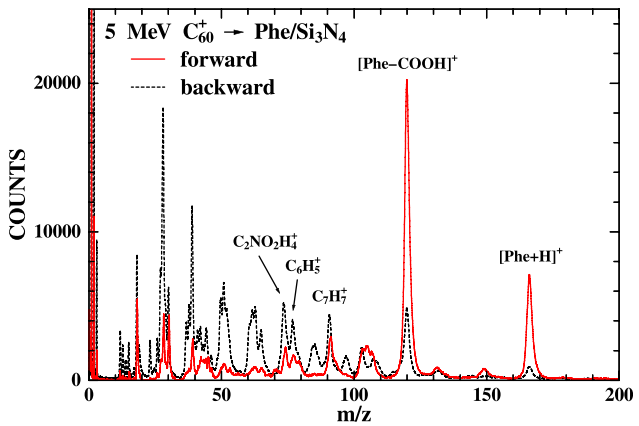

FIG. 5. Mass spectra for positive ions from phenylalanine films on a-Si_3N_4 films under 5 MeV C_{60}^{+} ion bombardment. The spectra observed in the forward direction (solid line) and the backward direction (dashed line) are shown.

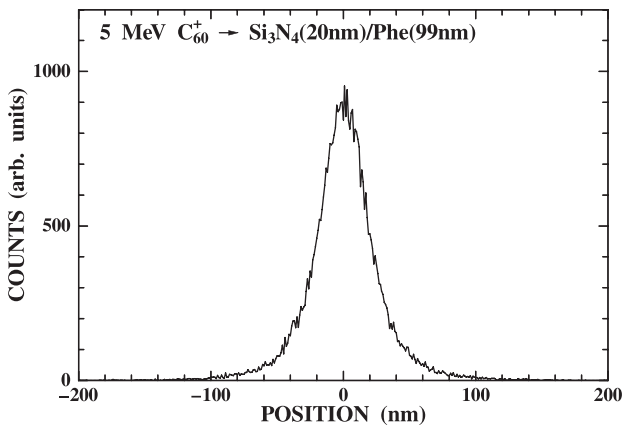

FIG. 6. Spatial distribution of constituent carbon ions at the exit surface when 5 MeV C_{60}^{+} incidents on a-Si_3N_4(20 nm)/phenylalanine(99 nm) films at an incident angle 45°.

In summary, secondary ions emitted from phenylalanine amino acid films were measured under bombardment of 5 MeV C_{60}^+ ions. The forward yield of the intact phenylalanine ion is about one order of magnitude larger than the backward direction. The fragment ions are suppressed in the forward direction compared to the backward direction and the degree of the suppression increases with decreasing mass number. The origin of these behaviors can be explained by the difference in the spatial distribution of the deposited energy between the entrance and exit surfaces. At the exit surface, a broader distribution with a low peak energy density is achieved. Such a distribution is preferable for the soft ionization which results in enhancement of the intact molecular ion emission and suppression of fragmentation. The present result suggests a large potential of using transmission cluster ion SIMS for the analysis of biological materials.

The authors are grateful to the crew of the 3 MV tandem accelerator at JAEA/Takasaki for providing the 5 MeV C_{60}^+ beam and to the members of the Quantum Science and Engineering Center of Kyoto University for the use of the tandetron accelerator. This work was partly supported by Grant-in-Aid for Exploratory Research from JSPS (Grant No. 24651114).

[1]L. A. McDonnell and R. M. A. Heeren, Mass Spectrom. Rev. **26**, 606 (2007).
[2]A. Brunelle and O. Laprevote, Curr. Pharm. Des. **13**, 3335 (2007).
[3]E. A. Schweikert, M. J. van Stipdonk, and R. D. Harris, Rapid Commun. Mass Spectrom. **10**, 1987 (1996).
[4]N. Toyoda, J. Matsuo, T. Aoki, I. Yamada, and D. B. Fenner, Appl. Surf. Sci. **203–204**, 214 (2003).
[5]K. Mori, D. Asakawa, J. Sunner, and K. Hiraoka, Rapid Commun. Mass. Spectrom. **20**, 2596 (2006).
[6]R. D. Rickman, S. V. Verkhoturov, E. S. Parillis, and E. A. Schweikert, Phys. Rev. Lett. **92**, 047601 (2004).
[7]K. Boussofiane-Baudin, A. Brunelle, P. Chaurand, S. Della-Negra, J. Depauw, P. Hakansson, and Y. Le Beyec, Nucl. Instrum. Methods Phys. Res. B **88**, 61 (1994).
[8]I. S. Bitensky and P. Sigmund, Nucl. Instrum. Methods Phys. Res. B **112**, 12 (1996).
[9]Y. Morita, K. Nakajima, M. Suzuki, K. Narumi, Y. Saitoh, W. Vandervorst, and K. Kimura, Nucl. Instrum. Methods Phys. Res. B **269**, 2080 (2011).
[10]A. Hedin, P. Hakansson, B. Sundqvist, and R. E. Johnson, Phys. Rev. B **31**, 1780 (1985).
[11]A. Hedin, P. Hakansson, M. Salehpour, and B. Sundqvist, Phys. Rev. B **35**, 7377 (1987).
[12]J. F. Ziegler, J. P. Biersack, and U. L. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).